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(54) Tanning leather

(57) Animal skins are treated in a bath containing a polyvalent metal salt and a polymer or oligomer containing carboxyl, carboxyl derivative or hydroxy functional groups capable of reacting with the polyvalent metal ion. The polyvalent metal is preferably aluminium or zirconium to obtain a

colourless finish, but if colour is not a problem, other metals such as chromium or iron may be used. The colour, or lack of it, is stabilised by the polyfunctional polymer or oligomer. Polymers or copolymer containing acrylic acid or maleic acid units may be used such as styrene-maleic acids copolymers, or suitably substituted cellulosic polymers such as sodium alginate.

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## SPECIFICATION

## Improvements in and relating to the manufacture of leather

This invention is concerned with the use of  
5 polyvalent metals as tanning agents in the manufacture of leather, particularly the use of aluminium salts.

Aluminium salts have been used in the manufacture of leather for some thousands of years, typically in the stabilising of animals skins by treatment with alum (potassium aluminium sulphate). However, the poor hydro-thermal stability of the product results in the traditional alum process being termed a "tawing" rather than a "tanning" process. Attempts have been made to increase the hydrothermal stability of the products of aluminium based skin treatments by using aluminium chlorides, or by using aluminium sulphate with organic acid anions, or the use of aluminium triformate, citrate etc, the effect being to increase the pH at which the aluminium salts precipitate. The maximum shrinkage temperatures (a measure of hydrothermal stability) obtained with these systems is about 80°C compared with 65 to 70°C obtained by alum tawing and about 60°C for untreated skins. (Shrinkage temperatures are determined by heating a skin sample in water and observing the temperature at which shrinkage occurs. Suitable procedure is set out in Method SLP 17 of the Society of Leather Technologists and Chemists). However these systems are not necessarily resistant to water (Williams-Wynn J. Soc. Leather. Tec. Chem.). In order to meet the requirements of modern foot ware manufacture or garment manufacture or renovation, it is desirable to attain shrinkage temperatures in excess of 100°C and preferably above 110°C to allow for some margin of safety to withstand the effects of steam.

It has also been proposed to use vegetable tannins (plant phenolics) with aluminium salts, but such processes lose the most desirable feature of alum tawing which is the lack of colour (whiteness) associated with the finished product.

We have developed a process for improving the stability of animal skins by treating the skins with a salt of a polyvalent metal and a polymer or oligomer containing carboxyl, carboxyl derivative or hydroxyl functional groups capable of reacting with the polyvalent metal ion.

As the preferred product of our process is a skin unchanged in colour by the treatment, the preferred polyvalent metal ion is aluminium. Other colourless polyvalent metal ions such as zirconium (IV), titanium (IV) and cerium (III) may also be used, alone or in conjunction with aluminium, e.g. as mixed complexes of aluminium-titanium, aluminium-zirconium. The use of basic aluminium salts derived from aluminium sulphate containing low molecular weight carboxylic or hydrocarboxylic acid ligands e.g. acetate, citrate, tartrate, has been found to give enhanced hydrolytic stability to the leather.

If lack of colour is not important, than other

65 polyvalent metal ions such as chromium (III), or iron (III), or aluminium-chromium complexes, can be used. Small amounts, not exceeding molar ratios of 1:5, of trivalent chromium added to aluminium, cerium, etc., give a pronounced and sometimes desirable blueing to the natural cream colour of the animal skin.

The special feature of the present process is that the colour, or lack of colour, is stabilized by use of a poly-functional organic polymer or oligomer which is itself inherently colourless or at least resistant to colour change on exposure to visible or ultra-violet light. Preferably the polymers or oligomers have a minimum of six functional groups per molecule, and a molecular weight in excess of 500. The poly-functional compounds may be present in aqueous solutions, dispersion or emulsion. They may be applied to the animals skins to be treated prior, subsequent to, simultaneously with, or previously reacted with the polyvalent metal salt. The polyvalent salt may itself contain ligands such as hydroxyl groups or anions of mono or polycarboxylic acids, but preferably has a molecular weight of less than 500.

As for the functional group containing polymer, we have found that useful results can be obtained with various proprietary acrylic polymers and styrene-maleic acid copolymers. Natural or chemically modified cellulosic polymers containing carboxyl groups may also be used, for example sodium alginate and carboxy methyl cellulose. The functional groups on the polymer or oligomer may include those giving rise to ampholytic properties through the incorporation of amine, amide, substituted amide (e.g. methylolamide) functions in order to improve reactions with anionic compounds and thus enhance surface colour after dyeing. The polymers may also contain reactive groups such as N-methylol capable of cross linking by thermal or acid catalysis, whether by means of pH adjustment or the presence of acidic, e.g. carboxyl, groups in the polymer.

Typical quantities of the tanning compounds used in the present process are from 0.5 to 20% by weight of aluminium based on dry skin protein weight. The quantity of polymer or oligomer solid is from 0.1 to 5 times the weight of aluminium offered to the skin protein.

The present process may also be used in conjunction with other conventional tanning systems, for example systems based on the use of aldehydes such as formaldehyde and glutaraldehyde.

The process of the present invention is illustrated by the following examples:

## EXAMPLE 1

100 g of dry skin protein was soaked in water and its pH adjusted to 4.5. 32 g of styrene maleic acid copolymer was dissolved in sufficient water to give a liquid to pelt ratio of 4:1 is then added and the pelt churned in the polymer solution for 60 minutes, after which the pH is progressively

reduced to 3.0 — 3.5 over a period of 90 minutes. The spent liquid is drained off, 7 g aluminium as the triformate is added, this being dissolved in 400 ml solution. After 2 hours, churning the pH is

5 raised to 4.0—4.5 by additions of sodium bicarbonate over a period of 60 minutes.

The leather has an aluminium content of 5—7%  $\text{Al}_2\text{O}_3$ , has a shrinkage temperature of 96—100°C and a lightfastness of >6 on the BSI

10 standard blue wool scale.

#### EXAMPLE 2

100 g of dry skin protein is prepared as in Example 1 and treated with 32 g of the solids contained in the proprietary product Retain 540 (Rohm & Haas Ltd.), in sufficient water to give a

15 liquid to pelt ratio 4:1. After 60 minutes the pH was progressively reduced to 3.0—3.5 by additions of formic acid. This liquid was drained

20 off and 6 g aluminium in the form of aluminium triformate added, after being dissolved in 400 ml

water, after churning for 2 hrs. 0.8 g chromium sesquioxide is added as the 33% basic chromium

25 sulphate. After 2 hrs the pH is adjusted to pH 4.0 by additions of sodium bicarbonate.

The resultant leather contained 3.9%  $\text{Al}_2\text{O}_3$  and 0.4%  $\text{Cr}_2\text{O}_3$ , had a shrinkage temperature of 100°C and a lightfastness on the blue wool scale of >6.

#### EXAMPLE 3

Pickled long wool sheepskin was washed in 6% brine solution and de-pickled with 4% sodium acetate trihydrate + 2% sodium bicarbonate in 3000% float. Agitation throughout the process was minimal to avoid felting the wool. After treatment over night at room temperature the solution pH was 6.2. The pelt was washed twice with water and then treated overnight with 3000% float containing 4 g of a copolymer of styrene and maleic acid. After acidification with sulphuric acid to pH 4.2, the pelt contained 3% of polymer, based on pickled weight. After washing the pelt was treated overnight with 3000% float containing 25 g  $\text{Al}_2\text{O}_3$ . The aluminium salt was the sulphate containing sodium acetate such that the

45 molar ratio  $\text{OAc}^- : \text{Al}_2\text{O}_3 = 0.5$  and made 33% basic by the addition of sodium carbonate. The pH of the float at the end of the treatment was 4.35 and was increased to 4.5 by the addition of sodium bicarbonate. The leather was toggle-dried

50 at room temperature.

The leather was neutralised to pH 6.5 with sodium carbonate and treated with 5% medium sulphited sperm oil for 60 min. at 50°C. The leather obtained in this way had a shrinkage temperature of 82°C and contained 3.90%  $\text{Al}_2\text{O}_3$  on oven-dried weight. After washing for five days with 3000% float at room temperature, 89% of the aluminium content remained in the leather.

In comparison substituting the 33% basic, 60 acetate-masked, aluminium tanning agent by

potash alum for the same tanning process, yielded leather from which 45% of the aluminium content was removed by washing with water for five days. Again using the same process, but masking the potash alum with sodium formate, such that the molar ratio formate:  $\text{Al}_2\text{O}_3 = 0.4$ , washing the leather for five days removed 26% of the aluminium content.

#### CLAIMS

70 1. A process for improving the stability of animal skins comprising treating the skins with a salt of a polyvalent metal and a polymer or oligomer containing carboxyl, carboxyl derivative or hydroxyl functional groups capable of reacting with the polyvalent metal ion.

75 2. A process according to Claim 1 in which the polymer or oligomer has a minimum of six functional groups per molecule and a molecular weight in excess of 500.

80 3. A process according to Claim 1 or 2 in which the polymer is a styrene-maleic acid copolymer.

4. A process according to Claim 1 or 2 in which the polymer is a polymer containing acrylic acid units.

85 5. A process according to Claim 1 or 2 in which the polymer is a cellulose polymer containing carboxyl groups.

90 6. A process according to Claim 5 in which the cellulosic polymer is sodium alginate or carboxyl methyl cellulose.

7. A process according to any preceding claim in which the polyvalent metal is aluminium.

8. A process according to Claim 7 in which the polyvalent metal salt is a basic aluminium salt derived from aluminium sulphate and containing a low molecular weight carboxylic or hydroxyl-carboxylic acid ligand.

9. A process according to any one of Claims 1 to 6 in which the polyvalent metal is zirconium (IV), titanium (IV) or cerium (III).

100 10. A process according to any one of Claims 1 to 6 in which the polyvalent metal is chromium (III) or iron (III).

105 11. A process according to any one of Claims 1 to 6 in which the polyvalent metal salt is a mixed complex of aluminium-titanium, aluminium-zirconium, or aluminium-chromium.

110 12. A process according to any one of Claims 7, 8 or 9 in which trivalent chromium is used with aluminium, zirconium (IV), titanium (IV) or cerium (III) in a molar ratio of not more than 1:5.

115 13. A process according to any one of the preceding claims in which the polymer or oligomer includes functional groups giving rise to ampholytic properties.

14. A process according to any one of the preceding claims in which the polymer or oligomer contains a reactive group capable of cross-linking by thermal or acid catalysis.

120 15. A method according to Claim 1 substantially as described in any one of the

## Examples.

16. An animal skin treated by a method according to any one of Claims 1 to 15.

17. An article made from an animal skin treated by a method according to any one of Claims 1 to 15.

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